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IMPROVED PREPARATION OF ACRYLIC RUBBER
Curing Methods and Properties of the Vulcanizates

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IMPROVED PREPARATION OF ACRYLIC RUBBER. CURING METHODS AND PROPERTIES OF THE VULCANIZATES

W. C. Mast and C. H. Fisher

INTRODUCTION

Several types of acrylic rubber have been made in this Laboratory by polymerizing acrylic esters (usually ethyl acrylate) and vulcanizing or cross linking the resulting acrylic polymers or copolymers (1-14).¹ Until recently, emulsion polymerization (15, 16) has been used here as a convenient method of preparing the elastomeric acrylic polymers of high molecular weight. The resulting polymers have been vulcanized² as follows: (a) Polymers such as ethyl polyacrylate have been cross-linked according to special recipes (5), which are discussed further below. (b) Unsaturated acrylic copolymers (prepared by polymerizing ethyl acrylate with a small amount of a polyolefinic monomer such as butadiene, isoprene, or allyl maleate) have been vulcanized with various agents, including sulfur and certain accelerators (6, 7, 10). (c) Halogen-containing copolymers, made conveniently by copolymerizing ethyl acrylate with a small proportion of monomers such as 2-chloroethyl vinyl ether and 2-chloroethyl acrylate, have been vulcanized with sulfur plus accelerators, amines, dioximes, metal oxides, and dinitrobenzene (1, 4, 5, 8).^{3,4} The vulcanization of a 95% ethyl acrylate-5% methyl vinyl ketone copolymer with various agents, including sulfur and accelerators, is described in this paper.

Some of the acrylic elastomers made as described above have excellent heat resistance (1-3, 14) and certain other outstanding properties (1). For example,

¹ THE PREPARATION OF SOMEWHAT SIMILAR ACRYLIC RUBBERS BY VULCANIZATION OF POLYACRYLIC ESTER WITH SPECIAL RECIPES (17-20) WAS ANNOUNCED RECENTLY BY THE B. F. GOODRICH CHEMICAL COMPANY (20, 21).

² THE TERM "VULCANIZATION" IS USED THROUGHOUT THIS PAPER IN THE BROAD SENSE, THAT IS, TO SIGNIFY CROSS LINKAGE IN GENERAL RATHER THAN IN THE LIMITED SENSE USED BY STIEHLER AND WAKELIN (22).

³ ETHYL ACRYLATE COPOLYMERS CONTAINING CYANO AND PHENOXY GROUPS ALSO HAVE BEEN VULCANIZED WITH SULFUR AND ACCELERATORS (5).

⁴ VULCANIZATION WITH NONSULFUR RECIPES HAS BEEN REVIEWED BY H. L. FISHER (23) AND ALFREY, HENDRICKS, HERSHEY, AND MARK (24).

the acrylic elastomer known as Lactoprene EV (95% ethyl acrylate-5% chloroethyl vinyl ether) is resistant at 300° F. for about 1,000 hours and at 400° F. for about 50 hours⁵. Because of the unusual properties and potential usefulness of these interesting elastomers, investigations in this field were extended in several directions. In one of these studies, an exceedingly simple method of preparing acrylic elastomers was found. The polymerization method, presumably applicable also to the preparation of various other polymers, is described, and the Lactoprene⁶ rubbers are reviewed briefly in the present paper. Inasmuch as there is considerable current interest (5, 17-21) in the vulcanization of polyacrylic esters, methods of curing ethyl polyacrylate and ethyl acrylate-methyl vinyl ketone copolymers also are discussed.

REVIEW OF PROPERTIES OF LACTOPRENE EV

Although ethyl polyacrylate can be cross-linked by certain special recipes, the chlorine-containing 95% ethyl acrylate-5% chloroethyl vinyl ether copolymer, designated Lactoprene EV, has been given much attention in vulcanization studies at the Eastern Regional Research Laboratory. Lactoprene EV was selected for such studies because of the ease with which it can be vulcanized with a variety of agents and the availability in large experimental quantities of the required chlorine-containing monomer, 2-chloroethyl vinyl ether.⁷

Although many recipes have been used to cure Lactoprene EV, greatest attention has been given to those that yield vulcanizates with excellent heat resistance. Many recipes based on sulfur plus accelerators have given heat-resistant vulcanizates. The sulfur-Monex-Trimene Base⁸ recipe listed below yielded vulcanizates having outstanding resistance to dry heat, that is, for approximately 1,000 hours at 300° F. and 50 hours at 400° F. Probably further study of the acrylic rubbers will develop products having even better heat resistance.

⁵ THIS COPOLYMER, ONCE MADE ON A PILOT PLANT SCALE BY THE OFFICE OF RUBBER RESERVE'S GOVERNMENT LABORATORIES IN AKRON (2, 25), IS NOW PREPARED IN LARGE EXPERIMENTAL QUANTITIES BY THE CHEMICAL ENGINEERING AND DEVELOPMENT DIVISION OF THE EASTERN REGIONAL RESEARCH LABORATORY (26). IT IS MADE COMMERCIALY BY THE B. F. GOODRICH CHEMICAL COMPANY, CLEVELAND, OHIO.

⁶ ACRYLIC RUBBERS HAVE BEEN CALLED 'LACTOPRENE' BECAUSE THE MONOMERIC ACRYLIC ESTERS CAN BE MADE EFFICIENTLY FROM LACTIC ACID (27, 28). LACTIC ACID (28) CAN BE MANUFACTURED FROM CARBOHYDRATES, PETROLEUM, NATURAL GAS, OR COAL.

⁷ CHLOROETHYL VINYL ETHER, SUPPLIED BY MERCK AND CO., INC., IN THE EARLIER STAGES OF THE INVESTIGATION, IS NOW OBTAINED FROM CARBIDE AND CARBON CHEMICALS CORPORATION. THE LATTER COMPANY IS CURRENTLY THE ONLY SOURCE OF THE ETHER KNOWN TO THE AUTHORS. CHLOROETHYL VINYL ETHER CAN BE MADE FROM INEXPENSIVE COMMERCIALY AVAILABLE CHEMICALS, I. E., 2-CHLOROETHYL ETHER AND ALKAL. (29, 30).

⁸ THE USE OR MENTION OF THIS AND OTHER SPECIFIC BRANDS OR COMMERCIAL PRODUCTS SHOULD NOT BE TAKEN AS A RECOMMENDATION OR ENDORSEMENT OF THESE PARTICULAR PRODUCTS OVER SIMILAR MATERIALS OR EQUIPMENT NOT MENTIONED.

	Parts
Lactoprene EV	100
SRF black ^a	50
Stearic acid	1
Tetramethylthiuram monosulfide (Monex) ^a	1
Trimene Base ^{b, c}	1 to 3
Sulfur ^a	2

^a Unpublished work by T. J. Dietz, J. E. Hansen, and P. E. Meiss of this Laboratory indicates that sulfur, tetramethylthiuram monosulfide, and SRF black each increase the water sensitivity of Lactoprene EV vulcanizates.

^b The larger quantities of Trimene Base given in the recipe may be used to accelerate the curing.

^c Chemical composition is given in Table I.

TABLE I. List of Emulsifiers and Compounding Ingredients^a

Trade Name	Chemical Name
Monex	Tetramethylthiuram monosulfide
Trimene Base	Triethyltrimethylenetriamine
Triton 720 ^b	Arylalkylpolyether sulfonate
Tergitol Penetrant Paste No. 4 ^b	Sodium tetradecylsulfate
Furnex	SRF carbon black
Accelerator 808	Butyraldehyde-aniline product
Kalvan	Coated calcium carbonate
Chloramine T	N-Chlorotoluenesulfonamide
Dichloramine T	N-Dichlorotoluenesulfonamide
Perchloron	Calcium hypochlorite
HTH	Calcium hypochlorite
Polyac	Nitroso compound ^c
Chloranil	Tetrachloro-p-quinone

^a Further information regarding compounding agents and sources of supply is given in India Rubber World, Compounding Ingredients for Rubber, Ed. 2, Conway Printing Co., New York. (1947).

^b Additional information on these detergents has been given by J. W. McCutcheon, (Synthetic Detergents Main Types, Uses, Properties and Prospects: Chem. Ind. 61: (5) 811 (November 1947)).

^c Described by B. M. Sturgis and J. H. Trepagnier, Rubber Age (N. Y.), 54: 325 (1944).

Other properties of the lactoprene rubbers may be illustrated by comparing their vulcanizates (1) with those made from GR-S, America's large-volume, general purpose synthetic rubber. Based on such a comparison, the advantages and disadvantages of lactoprene are summarized as follows:

COMPARISON OF LACTOPRENE EV WITH STANDARD GR-S RUBBER^a

Highly superior to GR-S with respect to:

1. Flex life.
2. Oil resistance.
3. Resistance to oxidation and aging at normal and elevated temperatures.^b
4. Resistance to sunlight.
5. Resistance to ozone

Superior with respect to:

1. Permeability to hydrogen, helium, and carbon dioxide.
2. Retention of elongation at high temperature.
3. Abrasion resistance (according to limited available data)
4. Ease and simplicity of production.
5. Yield from carbohydrate sources.
6. Suitability for production of white stocks or articles having pastel shades

Equal with respect to:

1. Ease of pigment incorporation.
2. Variety of curing recipes and rate of curing.
3. Retention of tensile strength at 212° F.
4. Permanent set.
5. Resilience at 212° F.

Inferior with respect to:

1. Tensile strength at normal temperatures (slight when compared with similarly loaded GR-S).
2. Retention of modulus at 212° F. (except in the longer cures).
3. Compression set (slight).
4. Heat build-up (except for higher cures).

^a The properties of Lactoprene EV and of GR-S have been summarized in Reference 1, 3, 11 and 13 and in Modern Plastics Encyclopedia, 1948, respectively.

^b In resistance to aging at elevated temperatures, Lactoprene EV vulcanizates are also highly superior to other elastomeric materials described in technical literature, except the silicones

5. Resilience at room temperature.
 6. Flexibility at low temperatures (but sufficiently flexible - if plasticized - at temperatures normal in civilian applications, i.e., to as low as about -35°C)
 7. Resistance to steam.
 8. Swelling in water (although undesirable for some applications, this characteristic might be advantageous for the manufacture of rubber sheets, shoes, garments, and similar products).
 9. Cost (acrylic esters are made on a relatively small scale, but it is expected that they will be made on a larger scale and as a result sold at much lower prices).
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The monomers used in preparing lactoprene are liquid at room temperature; hence pressure equipment is not required for polymerization or storage. The reaction progresses orderly, so that polymerization regulators or measures to prevent premature cross linkage are not required. Nor is it necessary to "short-stop" the polymerization; the reaction is carried to completion in a short time (one or two hours), and the yield of polymer is almost quantitative. Properties may be varied over a wide range by using various acrylic esters or by copolymerizing with other monomers. The crude polymer is soluble in many organic solvents, and therefore it is suitable for the preparation of coatings and adhesives. At least two separate curing mechanisms appear to be available for vulcanization, depending on the formulation employed; hence vulcanizates having various properties can be made by the proper selection of the recipe. White vulcanizates in particular and products having pastel shades are possible. Since no initial breakdown is required, the polymer is well suited to compounding in a Banbury mixer. Plasticizers and softeners are not required for compounding, although they may be used successfully if desired. The monomers can be made from petroleum, coal, or carbohydrates. One pound of carbohydrate yields approximately one pound of reinforced lactoprene vulcanizate.

Lactoprene naturally should prove most useful in fields in which its special properties are used to the maximum. Because of its excellent flex life, cut-growth resistance, and resistance to oils, oxidation, sunlight, ozone, and deterioration at normal and elevated temperatures, lactoprene should be useful, possibly preferable to other elastomers, for products such as hose, gaskets, and packings, transmission and conveyor belts, boots, soles, and heels which come in contact with oil or heat, tank linings where oil or high temperatures are encountered, printing rolls, white articles or articles having pastel shades, oil-resistant gloves and fabrics, machine and instrument supports, grommets, mats and pads, protective covers, cements, gasoline hose nozzles, coated cloth and paper (applied from solution or water emulsion), and laminated paper and cloth.

Lactoprene has been experimentally used as latex and as rubber cement. Hard rubberlike materials have been made from it. More data are needed, however, to evaluate the merit and possibilities of lactoprene in these fields.

PREPARATION OF ACRYLIC RUBBERS

One advantage of the lactoprene rubbers is the ease and convenience with which they can be made by emulsion polymerization. It has been pointed out previously that the preparation of acrylic rubber by emulsion polymerization (1, 15, 25, 26) is simpler than the similar preparation of many other elastomers for several reasons. Some of these are: 1. Less time (1 or 2 hours) is required for the polymerization. 2. Pressure reaction and storage vessels are not required. 3. Modifiers and antioxidants are not required. 4. The polymerization is not short-stopped, and the conversion into polymer is almost quantitative. Although the emulsion polymerization of acrylic esters is unusually convenient and the yield of polymer is almost quantitative, an even simpler method of preparing acrylic rubber has been found. Examples of both the new method⁹ and the emulsion polymerization are given below. Although the new method of polymerization appears superior for the preparation of the solid copolymer, the emulsion polymerization processes are of great interest because of the actual and potential importance of acrylic resin latices.

A. Emulsion Polymerization - A typical preparation of Lactoprene EV by emulsion polymerization is described below:

Ingredients	Parts
Water	200
Triton 720 ^{a, b}	1
Tergitol Penetrant Paste No. 4 ^{a, b}	1
Ethyl acrylate (monomer)	95
Chloroethyl vinyl ether	5
Ammonium persulfate	0.005

^a Moisture-free basis

^b See Table I.

The water and emulsifying agents were charged into the polymerization vessel, which was equipped with a stirrer, reflux condenser, and thermometer well. The monomer mixture and catalyst were then added, and the vessel was heated until refluxing occurred. The initial refluxing temperature was 82° C., and it rose to 95° C. at the end of the reaction. Heat was applied intermittently, if needed, to maintain refluxing. The reaction time was usually about 1 hour. The emulsion was then steam-distilled for 15 to 30 minutes to remove residual monomer. To obtain the solid copolymer, the hot emulsion was run slowly into twice its volume of hot (approximately 90° C.), rapidly stirred 5 percent sodium chloride solution.¹⁰ The precipitated polymer was washed with hot water until free of salt and dried. It was then ready for compounding, curing, and testing. If the emulsion was desired, it was cooled and poured into storage vessels.

⁹ THE NEW POLYMERIZATION METHOD AND VARIOUS MODIFICATIONS OF IT ARE BEING ACTIVELY INVESTIGATED HERE. THE RESULTS OBTAINED THUS FAR ARE PROMISING. THEY SHOW THAT THE NEW METHOD CAN BE USED TO ADVANTAGE IN THE PREPARATION OF MANY POLYMERS AND COPOLYMERS. A DESCRIPTION OF THE RESULTS OBTAINED IN THESE STUDIES WILL BE SUBMITTED FOR PUBLICATION.

¹⁰ POLYMER PRECIPITATED IN THIS MANNER WAS IN THE FORM OF DISCRETE PARTICLES AND WAS EASILY WASHED AND DRIED.

B. Granulation Polymerization¹¹ - The essential requirements of this process are water (in proportions varying from 10 to 60% of the total mixture) and suitable internal mixing. Unlike suspension polymerization, uninterrupted agitation is not required. The process is best illustrated by examples, and several are given below:

EXPERIMENT R-67

Ingredients	Parts
Ethyl acrylate monomer	95
Chloroethyl vinyl ether	5
Water	50
Ammonium persulfate	0.06

The ingredients listed above were charged into a Readco mixer equipped with sigma type blades, a reflux condenser, and a thermometer. The mixer was charged to approximately 50-60 percent of capacity. The order of charging was not important. Amounts of water from 10 percent to 60 percent of the charge have been used, and the essential feature of granulation was obtained in all instances. The mixture was heated to the refluxing temperature by passing steam through the jacket of the mixer. Refluxing was maintained by intermittent heating. During the reaction (100 minutes), the internal refluxing temperature rose 25° F. (the exact temperatures are not given, since they depend on the type of thermometer used and the extent of its immersion in the vapor phase).

At the end of the reaction, the material consisted of white, fluffy, granular particles that resembled boiled rice both in size and appearance. In this form the polymer was readily freed of monomer and dried. The dried polymer was also white, fluffy, and granular and had a tendency to cohere on standing. It was easily baled or compounded either on rubber mills or in Banbury mixers.

Although the mixer was fairly easy to clean after a run, a certain amount of polymer adhered to the blades and the sides of the vessel not immediately adjacent to the blades. The use of a lubricating agent during the polymerization considerably reduces the amount of material which clings to the vessel after a run and also promotes the formation of a more uniformly fine granular polymer. The lubricant should be insoluble in the monomer and water but dispersible in either. In the following example calcium stearate was used as a lubricant.

¹¹ BECAUSE THE POLYMER IS OBTAINED IN GRANULAR FORM, THE METHOD IS APTLY AND CONVENIENTLY TERMED 'GRANULATION POLYMERIZATION.' THE NEW METHOD, HOWEVER, SHOULD NOT BE CONFUSED WITH 'PEARL' OR 'SUSPENSION' POLYMERIZATION, WHICH EMPLOYS A LOWER MONOMER-TO-WATER RATIO AND IS USUALLY CARRIED OUT IN THE PRESENCE OF AGENTS SUCH AS BENTONITE OR TALC. SUSPENSION POLYMERIZATIONS USING UP TO 35 PERCENT OF ETHYL ACRYLATE MONOMER HAVE BEEN RUN HERE IN THE USUAL ROUND-BOTTOM GLASS FLASKS. THE POLYMER WAS OBTAINED AS A GRANULAR MATERIAL. THE GRANULES WERE SOMEWHAT LARGER THAN THOSE OBTAINED BY THE 'GRANULATION POLYMERIZATION' METHOD DESCRIBED ABOVE AND NOT SO AMENABLE TO REMOVAL OF MONOMER AND WATER. A CERTAIN PORTION OF THE POLYMER ALSO ADHERED TO THE FLASK.

EXPERIMENT R-74

Ingredients	Parts
Ethyl acrylate	95
Chloroethyl vinyl ether	5
Water	12.5
Calcium stearate	1
Potassium persulfate	0.0325

The mixture was heated to refluxing temperature by passing steam through the jacket. Refluxing was maintained by intermittent heating. During the polymerization (165 minutes) the internal refluxing temperature rose 25° F. The copolymer obtained was a white, fluffy, and granular material that resembled boiled rice. It was more uniformly fine than the material made in Experiment R-67 and less of it adhered to the sides and blades of the vessel. It was dried by passing steam-heated air through the mixer while it was running.

In other preparations the polymer was steam-stripped by passing steam through in a similar manner before drying. The polymerization has been carried out in a closed system, the temperature, time, and maximum pressure being, higher, shorter, and 10 pounds per square inch, respectively. The above copolymers were compounded and cured by a standard recipe. The physical properties of the vulcanizates are shown in Table 2, together with data from a typical Lactoprene EV made by emulsion polymerization.

For comparison, a batch of EV was prepared in the Readco Mixer without water:

EXPERIMENT R-68

Ingredients	Parts
Ethyl acrylate	95
Chloroethyl vinyl ether	5
Benzoyl peroxide	0.21

The mixture was heated, and polymerization was allowed to proceed for 60 minutes at 100° C. The resulting sticky copolymer was removed from the mixer in two large lumps that contained appreciable amounts of monomer. This material required additional treatment extending over a considerable time to remove the monomer and put it in a condition suitable for compounding.

Another example illustrating the preparation of ethyl polyacrylate by granulation polymerization is given below:

TABLE 2. PHYSICAL PROPERTIES OF LACTOPRENE EV VULCANIZATES^a

POLYMER NO.	EXPT. NO.	METHOD OF PREPARATION OF POLYMER	RAW MOONEY M-40	CURING TIME AT 298° F., MIN.	TENSILE STRENGTH, P. S. I.	MODULUS AT 200% P. S. I.	ULTIMATE ELONGA- TION, %	SHORE A HARDNESS	BASHORE REBOUND, %	AGED FOR 3 DAYS AT 300° F.			
										TENSILE STRENGTH, P. S. I.	MODULUS AT 200% P. S. I.	ULTIMATE ELONGA- TION, %	SHORE A HARDNESS
XP 101L ^c	2405B	EMULSION	52.8	30	1590	610	460	47		1690	1270	260	55
				60	1700	680	440	48		1630	1300	250	55
				120	1740	900	350	50		1530	1380	220	58
G-157 ^d	ES771	EMULSION	...	30	1700	460	640	49	1	1820	1365	280	59
				60	1740	560	560	49	1	1920	1520	260	58
				120	1890	610	550	50	1	1880	1570	250	60
R-68	2541	MASS	22.0	30, 60, 120 ^e									
R-67	2432	GRANULATION	...	60	1370	280	740	43
				120	1480	390	680	46		1660	620	420	45
R-74	2496 ^f	GRANULATION	57.8	30	1580	490	530	45	4	1650	1050	280	55
				60	1810	750	440	46	3	1670	1260	260	55
				120	1740	790	420	50	2	1690	1400	250	55
R-81 ^g	2512 ^f	GRANULATION	53.2	30	1670	590	490	46	3
				60	1805	710	475	48	3
				120	1900	880	415	49	3	1660	1500	225	55
R-84 ^h	2536 ^f	GRANULATION	54.1	30	1760	550	540	47
				60	1820	750	450	48
				120	1880	880	420	49		1815	1500	260	54

^a Recipe: 100 parts Lactoprene EV, 1 part tetramethyl thiuram monosulfide, 2 parts sulfur, 2 parts Trimene Base, and 50 parts SRF black.

^b Large rotor, 4 minutes.

^c Copolymer supplied by University of Akron Government Laboratories.

^d Copolymer was supplied by B. F. Goodrich Company; only 1 part of Trimene Base used.

^e Badly pitted; No evidence of cure.

^f Stearic acid, not required for processing, was omitted.

^g Made by granulation process, 3 parts calcium stearate used.

^h Made by granulation process, 1 part calcium stearate and 0.5 part stearic acid used.

EXPERIMENT R-87

Ingredients	Parts
Ethyl acrylate	100
Water	12.5
Potassium persulfate	.0375

The mixture was heated to the refluxing temperature, and refluxing was maintained by intermittent heating. During the reaction (115 minutes), the temperature rose 26° F. The product was steam-stripped for 10 minutes, with the mixer running, and then dried by blowing steam-heated air through (with the mixer running) for 20 minutes. A white, fluffy, granular polymer was obtained.

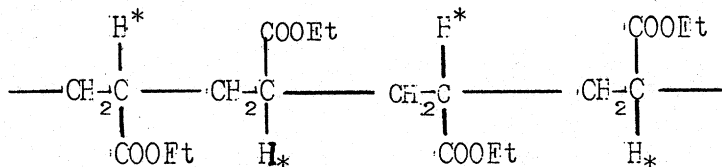
As judged by appearance, intrinsic viscosity, Mooney viscosity, curing rates, and physical properties of the vulcanizates, the granulation polymers appeared to be the equal of those made by emulsion polymerization (Table 2). The polymers made by the new process were apparently superior in some respects to the emulsion polymers.

Relatively little power was required for the granulation polymerization because the viscosity of the polymerizing mass was not excessive. Probably other types of mixer, including those of less rugged construction, can be used. As yet, the most suitable equipment, optimum conditions and preferred lubricants for operation on a large scale¹² have not been ascertained.

VULCANIZATION OF ACRYLIC ELASTOMERS

A. Ethyl Polyacrylate

It has been pointed out in previous publications that ethyl acrylate copolymers containing olefinic unsaturation (6, 7, 10) or halogen (5, 8) can be vulcanized readily with many agents, including sulfur and certain accelerators. Since attempts to cross link ethyl polyacrylate with many of these agents were unsuccessful (5, 8), the facile vulcanization of the copolymers has been attributed to the presence of olefinic linkages or halogen atoms. Although much attention has been given to the vulcanization of the reactive unsaturated and halogen-containing copolymers, the simple polymeric acrylic esters also have functional groups, and they also can be vulcanized or cross linked with certain agents (5, 17-21, 31, 32). The nature of the functional groups in the simple polymeric acrylic esters are indicated below with ethyl polyacrylate:

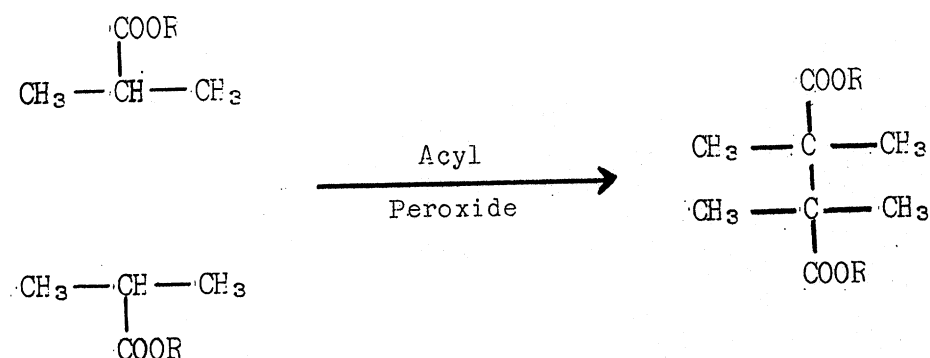


¹² THE MIXERS USED THUS FAR FOR THE GRANULATION POLYMERIZATIONS HAVE TOTAL CAPACITIES OF 1 AND 3 GALLONS; THEY WERE USED TO MAKE 4.5 AND 14 POUNDS OF POLYMER PER EXPERIMENT, RESPECTIVELY.

It would be expected from the structure of ethyl polyacrylate that cross linkage could be effected through either the ester groups or the alpha hydrogens (marked with an asterisk). Indeed, the vulcanization of ethyl polyacrylate through both reactive groups has been reported. The following are mentioned as examples of vulcanization through the ester group.¹³

- (a) Hydroxides of certain bivalent metals (1, 31) (presumably by hydrolysis of the ester and the formation of salts).¹⁴
- (b) Oxides of certain bivalent metals and stearic acid (1) (possibly by the acidolysis of the ester groups and subsequent formation of salts).¹⁴
- (c) Glycols (32) (presumably by alcoholysis, yielding cross-linked glycol diesters).
- (d) Ammonia and simple amines (33, 34) (presumably by the formation of amides followed by conversion into cross-linked imides (35)).

Probably the alpha hydrogens are involved in the cross linkage of ethyl polyacrylate and other polyacrylates with benzoyl peroxide (5) and with oxygen (36). This seems likely in view of the fact that acyl peroxides convert esters of isobutyric acid into esters of tetramethyl succinic acid (37, 38).



Isobutyric esters resemble ethyl polyacrylate in having a lone alpha hydrogen, and hence it is probable that the cross linkage of ethyl polyacrylate with benzoyl peroxide resembles the coupling of isobutyric esters. Presumably free radicals from sources other than benzoyl peroxide also could be used to cross link the polyacrylic esters.

The agents listed below also are capable of vulcanizing ethyl polyacrylate, but whether the vulcanization occurs through the ester group or the alpha hydrogen is not known.

¹³ BECAUSE OF STERIC HINDRANCE THE ESTER GROUPS OF ETHYL POLYACRYLATE WOULD BE EXPECTED TO REACT RELATIVELY SLOWLY.

¹⁴ CERTAIN STUDIES OF THIS TYPE WITH ETHYL POLYACRYLATE AND SIMILAR WORK WITH LACTOPRENE EV. MADE BY T. J. DIETZ AND J. E. HANSEN, AND MENTIONED EARLIER (1), HAVE NOT BEEN PUBLISHED.

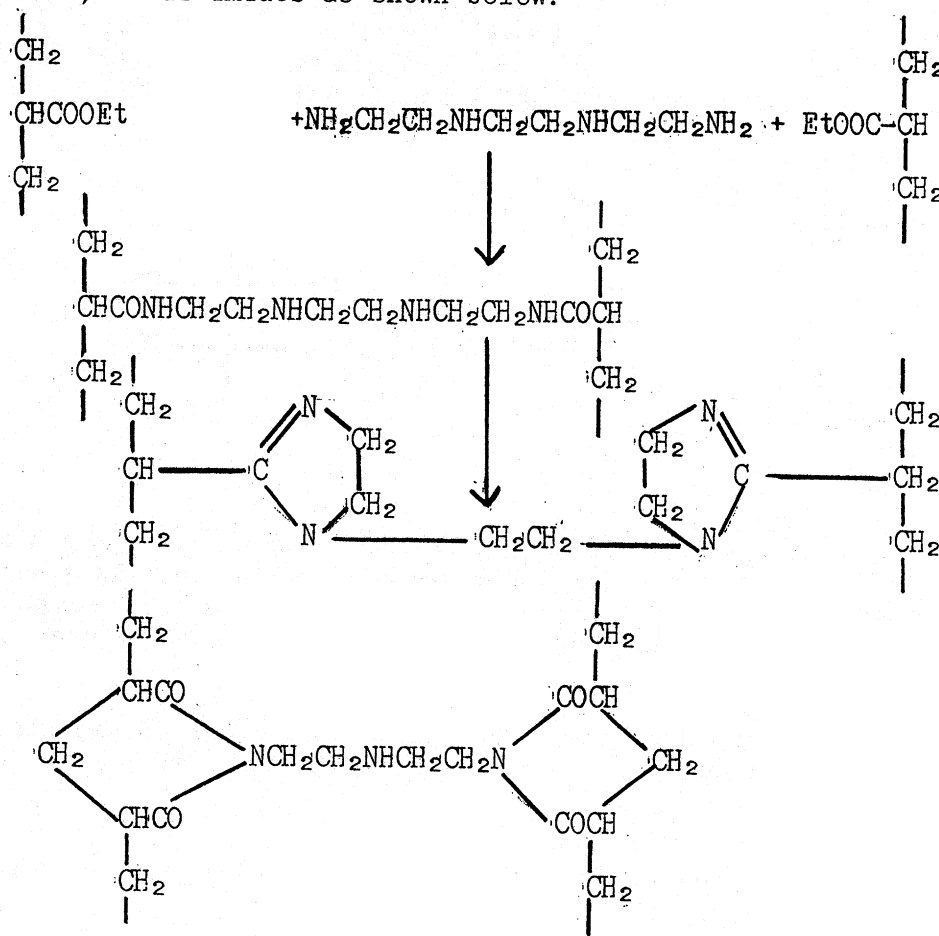
(a) Quinone dioxime and red lead or similar oxidants (5). According to Rehner and Flory (39), the reaction of dinitrosobenzene with olefinic linkages is responsible for curing Butyl rubber with quinone dioxime and oxidants.

(b) Litharge cures a "polyacrylic ester" of undisclosed composition (20). The litharge curing is accelerated by alkyl mercaptothiazoles (20).

(c) Sodium metasilicate has been used to cure a "polyacrylic ester" of undisclosed composition (20). Calcium hydroxide activates the sodium metasilicate (20).

(d) Sodium metastannate and sodium orthovanadate have been used to cure ethyl polyacrylate (18, 19).

Several additional methods may be used for the vulcanization of ethyl polyacrylate. One method is based on the use of triethylene tetramine (Table 3). Possibly cross linkage with this amine involves the formation of diamides, imidazoline, or di-imides as shown below:



Under the conditions used, the curing action of the triethylene tetramine was slow (Table 3, Expt. 2165). A mixture of triethylene tetramine and litharge had a more rapid curing action (Table 3, Expt. 2166) on ethyl polyacrylate.¹⁵ Litharge alone cured ethyl polyacrylate (Table 4), and therefore it is possible that vulcanization with the triethylene tetramine-litharge mixture occurred through at least two mechanisms, in which both agents functioned independently.

Litharge and Accelerator 808 (aniline-butyr-aldehyde product) also cured ethyl polyacrylate (Table 3, Expt. 2144). The vulcanizates prepared with this mixture of agents had relatively high tear strength and break set.

In several experiments (Table 5), chlorinating agents¹⁶ such as calcium hypochlorite were milled into polyethyl acrylate prior to the incorporation of cross linking agents. The polymer was rendered vulcanizable by the action of the chlorinating agent to the extent that sulfur plus accelerator recipes could be employed. Although vulcanization was achieved in some experiments, not enough work was done to determine the critical factor or factors responsible for the curing.

Ethyl polyacrylate was vulcanized successfully in 1 hour at 298° F. with a mixture of 2,6-dichloroquinonechloroimide and lead chromate (Table 5, Expt. 1800).

Several other recipes were tried without producing testable vulcanizates. These are described briefly below:

(a) Chloramine-T was milled into the cold polyethyl acrylate, which was then heated to 200° F. and milled for 10 minutes at that temperature. The resulting material was then compounded on cold rolls with 10 parts ZnO, 2 parts S, 0.5 part mercaptobenzothiazole, 1 part tetramethyl thiuramdisulfide, and 80 parts Kalvan. This experiment was repeated with one variation; the Chloramine-T was added to the polymer on hot rolls. Both these experiments were repeated with Dichloramine-T instead of Chloramine-T. In each instance the rubber failed to cure in 180 minutes at 298° F.

(b) HTH (calcium hypochlorite) and ammonium persulfate were milled into the cold polyethyl acrylate, which was heated to 200° F. and milled for 10 minutes at that temperature. The rubber was then compounded on cold rolls with 0.5 part

¹⁵ THE ETHYL POLYACRYLATE WAS PREPARED BY EMULSION POLYMERIZATION IN A 10-GALLON GLASS-LINED REACTION VESSEL BY THE CHEMICAL ENGINEERING AND DEVELOPMENT DIVISION OF THIS LABORATORY (26). THE COMPOUNDING INGREDIENTS IN THIS EXPERIMENT AND MOST OF THE OTHERS OF THE PRESENT WORK WERE MILLED INTO THE POLYMER WITH THE 'COLD-MILLING' TECHNIQUE PREVIOUSLY DESCRIBED (4). MILLING AT A HIGHER TEMPERATURE (ABOUT 160° F.) HAS BEEN USED IN PREFERENCE TO THE COLD-MILLING METHOD SINCE ABOUT 1946 (3).

¹⁶ RAINARD TREATED METHYL POLYACRYLATE WITH BROMINE AND VULCANIZED THE RESULTING PRODUCT WITH SODIUM SULFIDE (40)

TABLE 3. VULCANIZATION OF ETHYL POLYACRYLATE^{a, b, c, d}

Expt. No.	Parts per 100 parts of polymer			Curing time at 312° F. min.	Tensile strength, p.s.i.	Modulus, 400%	Ultimate elonga- tion, %	Shore A hardness	Crescent tear, p.s.i.	Break set, %
	Triethyl- tetramine	Litharge	Trimene Base							
2165 ^e	5	---	---	180	900	165	1100	33	127	12
2166 ^f	5	10	---	120	1350	860	650	40	180	11
2165 ^f	5	10	---	180	1480	1140	600	46	198	11
2143	---	10	5	180	---	---	---	---	---	---
2144	---	10	---	60	1450	690	860	45	291	43
2144	---	10	---	120	1650	1000	760	54	275	59
2144	---	10	---	180	1750	1120	700	56	279	66

a. All samples contained 100 parts ethyl polyacrylate (Preparation 40-18C15) and 30 parts SRP black; compounding was done on cold rolls.

b. Composition of agents is given in Table 1.

c. The Bashore rebound of the vulcanizates from Expts. 2165 and 2166 was 3 and 3.5%, respectively.

d. The vulcanizates from Expt. 2143 were pitted and unsuitable for testing.

e. After being oven aged at 300° F. for 3 days; Tensile strength, 1130 p.s.i.; modulus at 400%. 620 p.s.i.; elongation, 640%; and Shore A hardness, 35.

f. After being oven aged at 300° F. for 3 days; Tensile strength, 2050 p.s.i.; ultimate elongation, 250%; and Shore A hardness, 76.

TABLE II. VULCANIZATION OF ETHYL POLYACRYLATE WITH A LITHARGE RECIPE^a

	<u>Ethyl polyacrylate</u>	<u>(Expt. 2401)</u>	<u>Ethyl polyacrylate</u>	<u>(Expt. 2403)</u>
Plasticity, raw stock	61.8		51.4	
Cure at 310° F., min.	60	120	60	120
Tensile strength, p.s.i.	1180	1170	1240	1300
Modulus at 100%, p.s.i.	200	390	270	450
Ultimate elongation, %	610	440	510	380
Shore A hardness	45	55	53	58
Resilience, %	4	4	5	4
Brittle point, °C.		-10		-25
After aging for 3 days at 300° F.:				
Tensile strength, p.s.i.	1150	1260	1180	1240
Modulus at 100%, p.s.i.	820	940	1020	1160
Ultimate elongation, %	240	200	150	140
Shore A Hardness	70	75	80	80
Resilience, %	3	3	2	2

a. Recipe for acrylic polymer, 100 parts; litharge, 30; stearic acid, 3; and Furnex, 30.
A similar recipe was used earlier to vulcanize a polyacrylic ester (20).

TABLE 5. VULCANIZATION OF ETHYL POLYACRYLATE^a

Expt. No.	Stearic acid, parts	Chloramine T, parts ^b	Perchloron, Dichloramine T, parts ^b	Curing time at 312° F., min.	Tensile Strength, p.s.i.	Ultimate elongation, %	Shore A hardness
1792	2	--	--	180	--	--	--
1793 ^c	--	5	--	180	1100	860	58
1794 ^c	3	5	--	180	--	--	--
1806	--	5	--	180	--	--	--
1807	--	--	5	180	--	--	--
1808	2	--	5	180	--	--	--
1800 ^d	--	--	--	60 ^e	1060	540	40
1869 ^{f,g}	--	--	5	180	--	--	--
1870 ^f	--	--	5	60	700	1030	55

a. Recipe: 100 parts ethyl polyacrylate, 0.5 part 2-mercaptobenzothiazole, 10 parts zinc oxide, 2 parts sulfur, 1 part triethylene tetramine, 1 part tetramethyl thiuramdisulfide, and 30 parts SRF black.

b. In recipes using Chloramine T, Dichloramine T, or Perchloron, these chlorinating agents were milled into the rubber, which was then heated to 200-275° F. and milled at that temperature for 10 minutes. The rubber was then cooled, and the remaining ingredients added.

c. Kalvan (80 parts) used instead of 30 parts SRF black.

d. Recipe: 100 parts ethyl polyacrylate, 10 parts lead chromate, 5 parts 2,6-dichloroquinonechloroimide, and 30 parts SRF black.

e. Cured at 298° F.

f. Triethylene tetramine (2 parts) and Kalvan (80 parts) used instead of SRF black.

g. Sample cured, but the vulcanizate was pitted.

mercaptobenzothiazole, 2 parts sulfur, 5 parts MgO, 2 parts triethylene tetramine, 1 part tetramethyl thiuramdisulfide, and 30 parts SRF black. The experiment was repeated, with HTH, boric acid, and ammonium persulfate and again with HTH, boric acid and Dichloramine-T. In each experiment the mixture failed to cure after being heated for 180 minutes at 298° F.

(c) Several peroxides were also used as compounding ingredients without success. These were caprylyl peroxide, pelargonyl peroxide, sodium carbonate peroxide, and t-butyl hydroperoxide. These failed to produce curing in 60 minutes at 298° F.

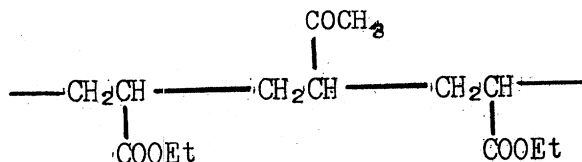
(d) The following combinations were also tried without producing vulcanizates suitable for testing:

1. 15 parts lead chromate plus 5 parts quinone chloroimide.
2. 15 parts lead chromate plus 5 parts 2,2',4,4' tetranitro diphenyl disulfide.
3. 15 parts red lead plus 5 parts chloranil.
4. 20 parts red lead plus 5 parts chloranil and 20 parts litharge.
5. 10 parts mercuric oxide plus 5 parts sym. di-betanaphthyl-para-phenylene-diamine.

Vulcanization did not occur in many of the experiments with ethyl polyacrylate, but several recipes produced cured specimens suitable for testing. Although much work would be required to demonstrate that these new vulcanizates are equal or superior to those made from the halogen-containing Lactoprene EV, it is of interest that ethyl polyacrylate can be vulcanized by many different recipes. Further efforts in this field might lead to superior vulcanizates and eliminate the need for introducing reactive vulcanizable groups by copolymerization. It seems likely, however, that the reactive copolymers such as Lactoprene EV will continue to be more versatile than ethyl polyacrylate with respect to amenability to vulcanization.

B. Ethyl Acrylate - Methyl Vinyl Ketone Copolymers

In view of the chemical reactivity of the methyl ketone group (—COCH_3) in both polymers (41) and compounds of relatively low molecular weight, copolymers of ethyl acrylate and methyl vinyl ketone were prepared and studied to ascertain the usefulness of the methyl ketone group for vulcanization purposes. The copolymers presumably had the structure shown below:



The methyl vinyl ketone segment resembles methyl isopropyl ketone in structure. Since methyl isopropyl ketone reacts readily with many reagents, it would be anticipated that the methyl ketone group in acrylic and other polymers would permit or facilitate cross linkage with various agents and mixtures.

The methyl vinyl ketone copolymers (Table 6) were not studied exhaustively, but it was demonstrated that two copolymers (95% ethyl acrylate - 5% methyl vinyl ketone and 90% ethyl acrylate - 10% methyl vinyl ketone) are amenable to vulcanization with the following agents.

- (a) sulfur plus certain accelerators
- (b) Quinone dioxime and red lead
- (c) Triethylene tetramine (Table 7)

The vulcanizates prepared in this brief study of the methyl vinyl ketone copolymers were not so heat resistant as those made from Lactoprene EV. These copolymers are of interest, however, because of their three functional groups (methyl ketone, ester, and alpha hydrogens) and the likelihood that they can be cross-linked with a variety of agents.

SUMMARY

An improved method for polymerizing monomers and preparing acrylic elastomers has been developed. The method, called "granulation polymerization," comprises polymerizing 100 parts of monomer with approximately 10 or more parts of water in a plastics mixer or similar suitable equipment. Although emulsifiers are not normally used, the polymer is obtained in small, discrete, granular particles. The polymer in this form can be dried and handled easily. The advantages of the new method over the conventional emulsion polymerization include the elimination or simplification of the coagulation, washing and drying operations.

Previously reported methods for vulcanizing ethyl polyacrylate and other simple polyacrylic esters are reviewed. Additional methods for cross linking ethyl polyacrylate are described.

The preparation and vulcanization of two ethyl acrylate-methyl vinyl ketone copolymers are described. These copolymers can be vulcanized with agents that are ineffective with ethyl polyacrylate, and hence the reactive methyl ketone group facilitates vulcanization.

These new data on the preparation and vulcanization of acrylic elastomers are of interest and importance because of the several outstanding properties of these elastomers and the commercial availability of elastomeric acrylic resins in both the solid and emulsified forms.

TABLE 6. EMULSION POLYMERIZATION OF ETHYL ACRYLATE AND METHYL VINYL KETONE.

Expt. No.	Methyl vinyl ketone, g.	Ethyl acrylate, g.	Water, ml.	Triton ^a 720, g.	Tergitol ^a penetrant, g.	Ammonium persulfate, g.	Polymerization time, min.	Polymerization temperature, °C.	Yield, %	Intrinsic viscosity of polymer ^b
E-192	10	90	200	1	0.75	0.005	45	79-90	88	3.29
E-193	5	95	200	1	.75	.005	42	81-91	92	4.04
M-131	40	760	1400	10	7.5	.040	82	81-91	--	--

a. Dry basis

b. Intrinsic viscosity calculated as $\ln \eta / c$

TABLE 7. VULCANIZATION OF METHYL VINYL KETONE COPOLYMERS^{a, b}

PHYSICAL PROPERTIES OF THE VULCANIZATES															
COPOLYMER NO.	EXPT. NO.	METHYL VINYL KETONE, %	RED LEAD, PARTS	ZINC OXIDE, PARTS	STEARIC ACID, PARTS	P. QUINONE DIOXIME, PARTS	TRIETHYLENE TETRAMINE, PARTS	MERCAPTO-BENZOTHI-AZOLE, PARTS	SULFUR, PARTS	TETRAMETHYL THURAMDI-SULFIDE, PARTS	CURING TIME AT 298°F., MIN.	OVEN AGED FOR 3 DAYS AT 300° F.			
												TENSILE STRENGTH, P.S.I.	SHORE A HARDNESS, %	ULTIMATE ELONGATION, %	SHORE A HARDNESS, %
E-192	1736	10	10	10	3	2					60	1470	64	300	64
											120	1650	69	270	69
											180	1790	68	230	68
E-192	1735	10		10	2			0.5	2	1	60	1090	42	850	42
											120	1340	45	800	45
											180	1370	47	670	47
E-193	1738	5	10	10	3	2					60	1400	55	550	55
											120	1580	64	370	64
											180	1640	68	290	68
E-193	1737	5		10	2			.5	2	1	60	940	39	940	39
											120	1040	43	760	43
											180	1010	42	610	42
M-131	2203	5		10	2			.5	2	1	30 ^d	1330	45	510	45
											60 ^d	1320	38	1140	38
											120 ^d	1540 ^e	41	750	41
AC79E33-2	2332	5					3				30	940	39	250	39
											60	1140	40	310	40
											120	1020	46	200	46
AC79E33-2	2470	5		10	2			1	2	1	120	1290	36	910	36
											180	1370	39	810	39

a. The copolymers were prepared by emulsion polymerization (Table 6); the following recipes did not cause vulcanization of the 5% methyl vinyl ketone copolymer after 120 minutes at 298°F. or 312°F.: A. 1 part stearic acid, 2 parts sulfur, 1 part tetramethyl thiuramdisulfide (312°F.); B. 10 parts litharge, 4 parts m-dinitro benzene (298°F.); C. 4 parts ammonium formate, 60 parts Kalvan (298°F.); D. 4 parts Polyac (298°F.); and E. 10 parts calcium oxide, 12 parts glyoxal sulfate (298°F.). All recipes included 30 parts SRP black except the one with 60 parts Kalvan.

b. Thirty parts of SRP black used with each sample.

c. Lead oxide, Pb₃O₄.

d. Curing temperature, 312°F.

e. Break set, 10%.

f. Break set, 3%.

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LITERATURE CITED

- 213 1. W. C. MAST, T. J. DIETZ, R. L. DEAN, AND C. H. FISHER, *Lactoprene EV Elastomer. Curing Recipes and Properties*. INDIA RUBBER WORLD 116, 355 (1947).
2. ANONYMOUS, *Acrylic Rubber Available*. CHEM. ENG. NEWS 25, 3238 (1947).
- 192 3. T. J. DIETZ, W. C. MAST, R. L. DEAN, AND C. H. FISHER, *Properties of Lactoprene EV*. IND. ENG. CHEM. 38, 960 (1946).
- 130 4. W. C. MAST, T. J. DIETZ, AND C. H. FISHER, *Rapid Vulcanization of Saturated Acrylic Elastomers*. INDIA RUBBER WORLD 113, 223 (1945).
- 75 5. W. C. MAST, C. E. REHBERG, T. J. DIETZ, AND C. H. FISHER, *Vulcanization of Saturated Acrylic Resins*. IND. ENG. CHEM. 36, 1022 (1944).
- 76 6. W. C. MAST, L. T. SMITH, AND C. H. FISHER, *Vulcanized Acrylic Resins. Copolymers of Ethyl Acrylate and Allyl Maleate*. IND. ENG. CHEM. 36, 1027 (1944).
- 71 7. C. H. FISHER, W. C. MAST, C. E. REHBERG, AND L. T. SMITH, *Lactoprene. New Synthetic Rubber*. IND. ENG. CHEM. 36, 1032 (1944).
- 251 8. W. C. MAST AND C. H. FISHER, *Vulcanization of Chlorine-Containing Acrylic Elastomers*. IND. ENG. CHEM. 40, 107 (1948).
9. W. C. MAST AND C. H. FISHER, *Properties of Lactoprene EV. Effect of Plasticizers*. PRESENTED BEFORE THE DIVISION OF RUBBER CHEMISTRY AT THE SEPTEMBER 1947 MEETING OF THE AMERICAN CHEMICAL SOCIETY, NEW YORK, N. Y.
- 344 10. W. C. MAST AND C. H. FISHER, *Preparation and Vulcanization of Unsaturated Acrylic Elastomers*. IN PRESS.
11. H. M. LEEPER, *Lactoprene E170*. 8 PP., JAN. 30, 1945, OFFICE OF RUBBER RESERVE, GOVERNMENT EVALUATION LABORATORIES, AKRON, OHIO.
12. H. M. LEEPER, *Lactoprene EV*. 12 PP., FEB. 6, 1946, OFFICE OF RUBBER RESERVE, THE UNIVERSITY OF AKRON GOVERNMENT LABORATORIES.
13. H. M. LEEPER, *Lactoprene - II*. AU-188, MAY 27, 1946, OFFICE OF RUBBER RESERVE, THE UNIVERSITY OF AKRON GOVERNMENT LABORATORIES.
14. R. B. MESROBIAN AND A. V. TOBOLSKY, *Some structural and Chemical Aspects of Aging and Degradation of Vinyl and Diene Polymers*. J. POLYMER SCI. 2, 463 (1947).
- 243 15. W. C. MAST AND C. H. FISHER, *Emulsion Polymerization of Acrylic Esters and Certain Other Vinyl Monomers*. TO BE PUBLISHED IN IND. ENG. CHEM.
- 131 16. W. C. MAST, L. T. SMITH AND C. H. FISHER, *Emulsion Polymerization of Acrylic Esters*. IND. ENG. CHEM. 37, 365 (1945).
17. S. T. SEMEGEN (TO THE B. F. GOODRICH COMPANY). *Treatment of Acrylic Ester Polymers*. U.S. PATENT 2,411,899 (DECEMBER 3, 1946).
18. S. T. SEMEGEN (TO THE B. F. GOODRICH COMPANY). *Treatment of Acrylic Ester Polymers*. U.S. PATENT 2,412,475 (DECEMBER 10, 1946).
19. S. T. SEMEGEN (TO THE B. F. GOODRICH COMPANY). *Treatment of Acrylic Ester Polymers*. U.S. PATENT 2,412,476 (DECEMBER 10, 1946).
20. ANONYMOUS, *Polyacrylic Ester - Experimental Product*. SERVICE BULLETIN 47-SD3. 10 PP. JULY 1, 1947. B. F. GOODRICH CHEMICAL COMPANY, CLEVELAND, OHIO.
21. ANONYMOUS (*Ilycar PA*), CHEM. ENG. NEWS 26, 405 (1948).
22. R. D. STIEHLER AND J. H. WAKELIN, *Mechanism and Theory of Vulcanization*. IND. ENG. CHEM. 39, 1647 (1947).

23. H. L. FISHER. *Vulcanization of Rubber*. IND. ENG. CHEM. 31, 1381 (1939).
24. T. ALFREY, J. G. HENDRICKS, R. M. HERSHEY, AND H. MARK. *Non-Sulphur Vulcanization*. INDIA RUBBER WORLD 112, 577, 738 (1945); AND 113, 653 (1946).
25. G. E. ALDEN. *Copolymerization of Ethyl Acrylate with Chloroethyl Vinyl Ether in the Production of Lactoprene EV*. AU. 521. 31 PP. FEBRUARY 20, 1948. OFFICE OF RUBBER RE-SERVE, THE UNIVERSITY OF AKRON GOVERNMENT LABORATORIES.
26. W. W. HOWERTON. *General Operating Conditions for Producing Lactoprene EV*. EASTERN REGIONAL RESEARCH LABORATORY (UNPUBLISHED REPORT).
27. L. T. SMITH, C. H. FISHER, W. P. RATCHFORD, AND M. L. FEIN. *Pyrolysis of Lactic Acid Derivatives. Conversion of Methyl Acetoxypropionate to Methyl Acrylate*. IND. ENG. CHEM. 34, 473 (1942).
28. C. H. FISHER AND E. M. FILACHIONE. *Lactic Acid - Versatile Intermediate for the Chemical Industry*. U. S. DEPARTMENT OF AGRICULTURE AIC-178, (1948).
29. C. E. REHBERG. *Research Report* (UNPUBLISHED).
30. W. CHALMERS. *Preparation of the Ethers of Vinyl Alcohol*. CAN. J. RESEARCH 7, 464 (1932).
31. F. C. ATWOOD AND H. A. HILL. (TO NATIONAL DAIRY PRODUCTS CORPORATION) *Elastic Alkyl Acrylate Polymers*. U. S. PATENT 2,398,350 (APRIL 16 1946).
32. F. C. ATWOOD (TO NATIONAL DAIRY PRODUCTS CORPORATION). *Polymers of Alkyl Acrylates*. U. S. PATENT 2,400,477 (MAY 21, 1946).
33. I. G. FARBEN. A. G. *Synthetic Resins*. BRIT. PATENT 450,692 (JULY 23 1936) (CHEM ABSTRACTS 31, 180 (1937)).
34. G. D. GRAVES (TO E. I. DU PONT DE NEMOURS & COMPANY). *Preparation of Resinous Imides of Substituted Acrylic Acids*. U. S. PATENT 2,146,209 (FEBRUARY 7, 1939).
35. H. STAUDINGER AND E. URECH. *Polyacrylic Acid and Polyacrylic Esters*. HELV. CHIM. ACTA 12, 1107 (1929).
36. C. E. REHBERG, AND W. A. FAUCETTE. *Preparation of Monomeric and Polymeric Acrylic Esters of Glycol Monoethers. Air-Induced Cross-Linkage of Polymeric Alkoxyethyl Acrylate Films*. PRESENTED BEFORE THE DIV. S ON OF PAINT VARN SH AND PLASTICS CHEM-ISTRY AT THE APRIL 1946 MEETING OF THE AMERICAN CHEMICAL SOCIETY, ATLANTIC CITY, N.J.
37. M. S. KHARASCH AND M. T. GLADSTONE. *Decomposition of Acetyl Peroxide in Aliphatic Acids - A New Synthesis of Succinic Acid and its Substitution Derivatives*. J. AM. CHEM. SOC. 65, 15 (1943).
38. B. S. BIGGS, R. H. ERICKSON, AND C. S. FULLER. *Rubberlike Products from Linear Poly-esters*. IND. ENG. CHEM. 39, 1090 (1947).
39. J. REHNER, JR. AND P. J. FLORY. *Vulcanization Reactions in Butyl Rubber. Action of Dinitroso, Dioxime, and Related Compounds*. IND. ENG. CHEM. 38, 500 (1946).
40. L. W. RAINARD (TO NATIONAL DAIRY PRODUCTS CORPORATION). *Method of Curing Acrylate Polymers*. U. S. PATENT 2,410,103 (OCTOBER 29, 1946).
41. C. S. MARVEL AND C. L. LEVESQUE. *Some Reactions of the Polymer of Methyl Vinyl Ketone*. J. AM. CHEM. SOC. 61, 3234 (1939).